Complex Interactions between Mercury (Hg) and Natural Organic Matter and Microorganisms on Hg Redox Transformation in Anoxic Environments

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Redox transformation of mercury (Hg) critically controls the Hg speciation and subsequently its bioavailability and microbial uptake for methylation. However, mechanisms by which Hg transforms in anoxic water and sediments remain poorly understood. In this presentation, we describe the multi-functional roles and processes of naturally dissolved organic matter (DOM) and methylating bacteria on Hg reduction, complexation, and oxidation. For DOM, Hg reduction and oxidation was found to be strongly influenced by both the oxidation state of sulfur in DOM and its ratio to Hg. Under dark, anaerobic conditions, the reduced DOM is capable of rapidly reducing Hg(II) to gaseous Hg(0) at a low DOM/Hg ratio but, at a high DOM/Hg ratio, this reaction is reversed due to thiol-ligand induced oxidative complexation of Hg(0). Similarly to DOM, certain strains of microorganisms such as *G. sulfurreducens* PCA are able to reduce Hg(II) at relatively low cell biomass:Hg(II) ratios, but the reduction becomes inhibited at increasing cell:Hg(II) ratios due to an increased surface complexation between Hg(II) and sulfhydryl functional groups on the cell outer membrane. An optimal reduction of Hg(II) was observed at a cell density of ~ 10^{11} L^{-1} and a fixed Hg(II) concentration of 50 nM. However, depending on specific surface functional properties and biochemical mechanisms, certain strains of microorganisms such as *D. desulfuricans* ND132 are incapable of reducing Hg(II) but are able to oxidize Hg(0) to Hg(II) species under strict anaerobic incubations. We attribute this oxidation to strong binding between Hg(0) and reduced sulfhydryl functional groups on the cell surface leading to oxidative complexation. This research highlights complex interactions and competing processes (e.g., reduction, oxidation, complexation or adsorption) that are likely occurring in anoxic water and sediments and thus may greatly influence the biological uptake of Hg(II) that leads to the formation of toxic methylmercury.